

Poly[[diaquabis[μ -2-(4-fluorophenoxy)-acetato- $\kappa^2 O^1 : O^{1'}$]magnesium] 0.4-hydrate]

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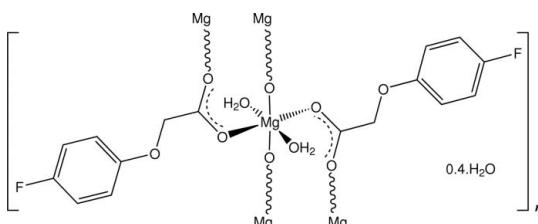
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Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(C-C) = 0.004$ Å; disorder in solvent or counterion; R factor = 0.047; wR factor = 0.109; data-to-parameter ratio = 13.2.

In the title compound, $\{[\text{Mg}(\text{C}_8\text{H}_6\text{FO}_3)_2(\text{H}_2\text{O})_2]\cdot 0.4\text{H}_2\text{O}\}_n$, slightly distorted octahedral MgO_6 complex units have crystallographic inversion symmetry, the coordination polyhedron comprising two *trans*-related water molecules and four carboxyl O-atom donors, two of which are bridging. Within the two-dimensional complex polymer which is parallel to (100), coordinating water molecules form intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds with carboxylate and phenoxy O-atom acceptors, as well as with the partial-occupancy solvent water molecules.

Related literature

For the structures of some magnesium complexes, derived from phenoxyacetic acids, see: Smith *et al.* (1980, 1981, 1982); Kennard *et al.* (1986). For the structures of other metal complexes with 4-fluorophenoxyacetate, see: O'Reilly *et al.* (1984); Smith *et al.* (1993).



Experimental

Crystal data

 $[\text{Mg}(\text{C}_8\text{H}_6\text{FO}_3)_2(\text{H}_2\text{O})_2]\cdot 0.4\text{H}_2\text{O}$
 $M_r = 405.80$

Monoclinic, $P2_1/c$
 $a = 17.2526(9)$ Å

 $b = 6.8899(3)$ Å

 $c = 7.5474(3)$ Å

 $\beta = 95.118(4)^\circ$
 $V = 893.57(7)$ Å³
 $Z = 2$

Mo $K\alpha$ radiation

 $\mu = 0.17$ mm⁻¹
 $T = 200$ K

 $0.30 \times 0.20 \times 0.05$ mm

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer

Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2012)

 $T_{\min} = 0.964$, $T_{\max} = 0.980$

5825 measured reflections

1762 independent reflections

1400 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.109$
 $S = 1.06$

1762 reflections

133 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.25$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.29$ e Å⁻³
Table 1

Selected bond lengths (Å).

$\text{Mg1}-\text{O1W}$	2.1032 (14)	$\text{Mg1}-\text{O22}^{\text{i}}$	2.0620 (14)
$\text{Mg1}-\text{O21}$	2.0478 (14)		

Symmetry code: (i) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$
Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1W}-\text{H11W}\cdots\text{O1}^{\text{iv}}$	0.91	2.45	3.214 (2)	143
$\text{O1W}-\text{H12W}\cdots\text{O22}^{\text{iv}}$	0.92	2.38	3.0352 (19)	128
$\text{O1W}-\text{H12W}\cdots\text{O21}^{\text{i}}$	0.92	1.92	2.760 (2)	151
$\text{O2W}-\text{H21W}\cdots\text{O1}^{\text{iv}}$	0.95	2.41	3.034 (10)	123
$\text{O2W}-\text{H22W}\cdots\text{O22}^{\text{iii}}$	0.85	2.13	2.950 (9)	160

Symmetry codes: (i) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (iv) $x, y + 1, z$.

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 1999); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5512).

References

- Agilent (2012). *CrysAlis PRO*. Agilent Technologies Ltd, Yarnton, England.
- Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Kennard, C. H. L., O'Reilly, E. J., Schiller, S., Smith, G. & White, A. H. (1986). *Aust. J. Chem.* **39**, 1823–1832.
- O'Reilly, E. J., Smith, G. & Kennard, C. H. L. (1984). *Inorg. Chim. Acta*, **90**, 63–71.
- Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.
- Smith, G., Lynch, D. E., Mak, T. C. W., Yip, W.-H. & Kennard, C. H. L. (1993). *Polyhedron*, **12**, 203–208.
- Smith, G., O'Reilly, E. J. & Kennard, C. H. L. (1980). *J. Chem. Soc. Dalton Trans.*, pp. 2462–2466.
- Smith, G., O'Reilly, E. J. & Kennard, C. H. L. (1981). *Cryst. Struct. Commun.* **10**, 1397–1402.
- Smith, G., O'Reilly, E. J. & Kennard, C. H. L. (1982). *Inorg. Chim. Acta*, **62**, 241–246.
- Spek, A. L. (2009). *Acta Cryst. D* **65**, 148–155.

supplementary materials

Acta Cryst. (2012). E68, m1178 [doi:10.1107/S1600536812035246]

Poly[[diaquabis[μ -2-(4-fluorophenoxy)acetato- $\kappa^2O^1:O^{1'}$]magnesium] 0.4-hydrate]

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Comment

Magnesium complexes involving monoanionic phenoxyacetate ligands (L) show a variety of coordination modes, all based on an octahedral MgO_6 metal stereochemistry, *e.g.* discrete monomeric $[[MgL_2(H_2O)_4]]$ (L = 2-fluorophenoxyacetate) (Kennard *et al.*, 1986); (L = 4-chloro-2-methylphenoxyacetate) (Smith *et al.*, 1981); $[MgL(H_2O)_5]$ (L = 2,4,5-trichlorophenoxyacetate) (Smith *et al.*, 1982)], or polymeric $[[MgL_2(H_2O)_2]_n]$ (L = phenoxyacetate or 4-chlorophenoxyacetate) (Smith *et al.*, 1980)].

The title complex, $[Mg(H_2O)_2(C_8H_6FO_3)_2]_n$ ($0.4H_2O$) $_n$ was obtained from the reaction of 4-fluorophenoxyacetic acid with $MgCO_3$ in aqueous ethanol and the structure is reported herein. In this structure (Fig. 1), the slightly distorted octahedral MgO_6 complex units [bond range Mg—O, 2.0478 (14)–2.1032 (14) Å (Table 1)] have crystallographic inversion symmetry, the coordination polyhedron comprising two *trans*-related water molecules and four carboxyl O-atom donors, two of which are bridging. Within the two-dimensional complex polymer layers which extend across (100), the coordinated water molecules from intermolecular O—H \cdots O hydrogen-bonding interactions (Table 2), with carboxyl and phenoxy O-atom acceptors as well as with the partial water molecules of solvation (S.O.F. = 0.2) (Fig. 2). Except for the presence of the partial water molecules, the structure is similar to those of the isomorphous Mg complexes with phenoxyacetate and 4-chlorophenoxyacetate (Smith *et al.*, 1980). In the present complex, the 4-fluorophenoxyacetate ligand is essentially planar, with the carboxyl group rotated slightly out of the plane [benzene ring to acetate dihedral angle = 12.26 (12)°].

Experimental

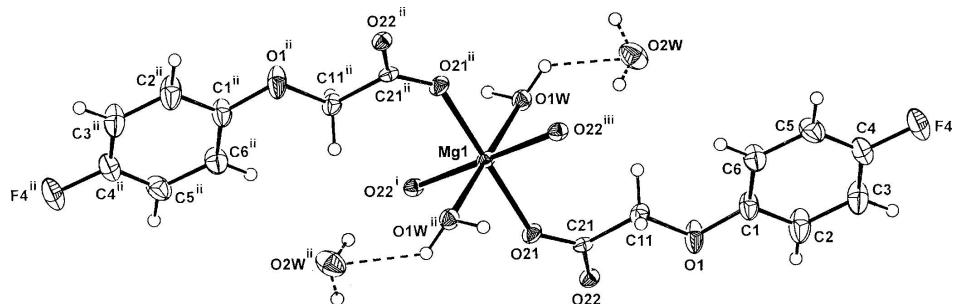
The title compound was synthesized by the addition of excess $MgCO_3$ to 15 ml of a hot aqueous ethanolic solution (10:1) of 4-fluorophenoxyacetic acid (0.1 g). After completion of the reaction, the excess $MgCO_3$ was removed by filtration and the solution was allowed evaporate to incipient dryness at room temperature, giving thin colourless plates of the title compound from which a specimen was cleaved for the X-ray analysis.

Refinement

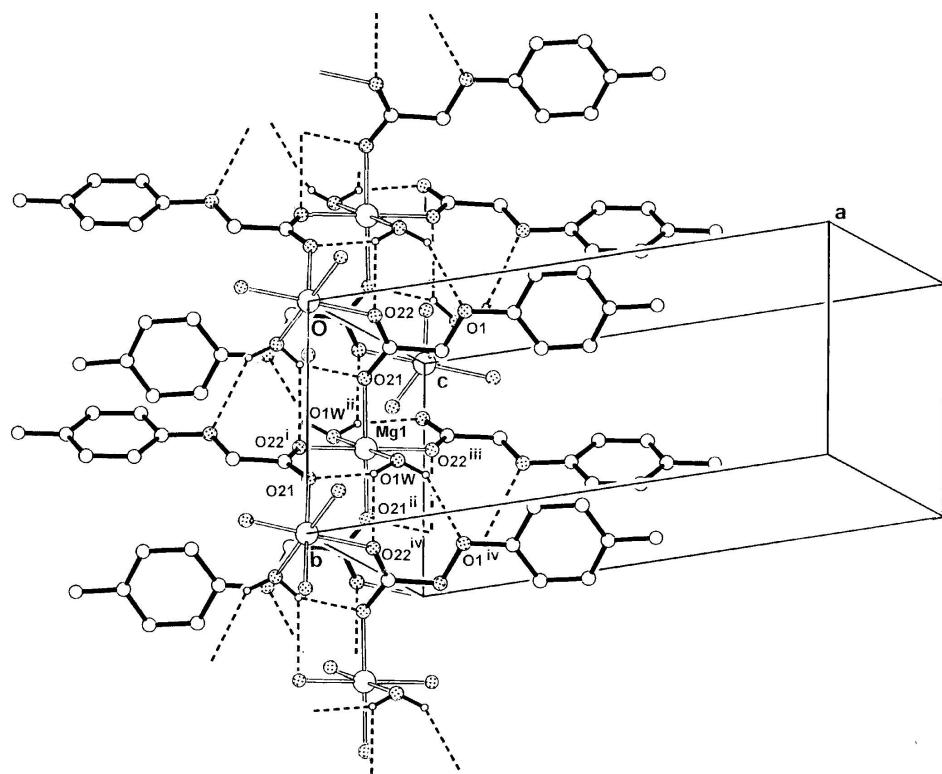
Hydrogen atoms on the coordinated water molecule were located by difference methods and both positional and isotropic displacement parameters were initially refined but these were then allowed to ride, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. Other H-atoms were included in the refinement at calculated positions [$\text{C}—\text{H}(\text{aromatic}) = 0.93$ Å, 0.98 Å (methylene)] or $\text{O}—\text{H} = 0.84$ –0.94 Å, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{O})$, also using a riding-model approximation. The site occupancy factor for the partial water molecule of solvation was determined as 0.196 (4) and was subsequently fixed as 0.20.

Computing details

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO* (Agilent, 2012); data reduction: *CrysAlis PRO* (Agilent, 2012); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 1999); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON* (Spek, 2009).

**Figure 1**

The molecular structure of the title compound, including the partial water molecules of solvation (O_2W), with displacement ellipsoids drawn at the 50% probability level. For symmetry codes, see Table 1.

**Figure 2**

The hydrogen-bonding interactions, shown as dashed lines, in the title compound viewed along c . The partial water molecule of solvation and non-associative H-atoms have been omitted. For symmetry codes, see Tables 1 and 2.

Poly[[diaquabis[μ -2-(4-fluorophenoxy)acetato- κ^2 O¹:O^{1'}]magnesium] 0.4-hydrate]*Crystal data* $[\text{Mg}(\text{C}_8\text{H}_6\text{FO}_3)_2(\text{H}_2\text{O})_2] \cdot 0.4\text{H}_2\text{O}$ $M_r = 405.80$ Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

 $a = 17.2526 (9)$ Å $b = 6.8899 (3)$ Å $c = 7.5474 (3)$ Å $\beta = 95.118 (4)^\circ$ $V = 893.57 (7)$ Å³ $Z = 2$ $F(000) = 420$ $D_x = 1.508 \text{ Mg m}^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1476 reflections

 $\theta = 3.2\text{--}28.9^\circ$ $\mu = 0.17 \text{ mm}^{-1}$ $T = 200$ K

Plate, colourless

 $0.30 \times 0.20 \times 0.05$ mm*Data collection*Oxford Diffraction Gemini-S CCD-detector
diffractometer

Radiation source: Enhance (Mo) X-ray source

Graphite monochromator

Detector resolution: 16.077 pixels mm⁻¹ ω scansAbsorption correction: multi-scan
(*CrysAlis PRO*; Agilent, 2012) $T_{\min} = 0.964$, $T_{\max} = 0.980$

5825 measured reflections

1762 independent reflections

1400 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.040$ $\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 3.2^\circ$ $h = -21 \rightarrow 21$ $k = -8 \rightarrow 8$ $l = -9 \rightarrow 9$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.047$ $wR(F^2) = 0.109$ $S = 1.06$

1762 reflections

133 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 0.393P]$
where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$ *Special details*

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Mg1	0.00000	0.50000	0.50000	0.0187 (3)	
F4	0.49577 (8)	-0.0237 (3)	0.7819 (2)	0.0567 (6)	
O1	0.20100 (10)	-0.0103 (3)	0.4489 (2)	0.0481 (6)	
O1W	0.09125 (8)	0.6177 (2)	0.36712 (19)	0.0255 (5)	
O21	0.01967 (8)	0.2303 (2)	0.39916 (19)	0.0255 (4)	

O22	0.07774 (8)	0.02846 (19)	0.22234 (18)	0.0220 (4)	
C1	0.27377 (13)	-0.0045 (4)	0.5408 (3)	0.0358 (8)	
C2	0.32768 (15)	-0.1323 (4)	0.4814 (4)	0.0519 (10)	
C3	0.40282 (15)	-0.1370 (4)	0.5616 (4)	0.0487 (9)	
C4	0.42218 (13)	-0.0158 (4)	0.7001 (3)	0.0393 (8)	
C5	0.37063 (15)	0.1118 (4)	0.7620 (3)	0.0408 (9)	
C6	0.29510 (14)	0.1183 (4)	0.6810 (3)	0.0378 (8)	
C11	0.14596 (12)	0.1286 (3)	0.4960 (3)	0.0264 (7)	
C21	0.07588 (12)	0.1271 (3)	0.3609 (3)	0.0194 (6)	
O2W	0.2262 (5)	0.5768 (14)	0.5816 (12)	0.048 (3)	0.200
H2	0.31330	-0.21540	0.38700	0.0620*	
H3	0.43940	-0.22160	0.52140	0.0580*	
H5	0.38580	0.19330	0.85700	0.0490*	
H6	0.25920	0.20490	0.72100	0.0450*	
H11A	0.16940	0.25660	0.50070	0.0320*	
H11B	0.12990	0.09860	0.61290	0.0320*	
H11W	0.13290	0.67830	0.42470	0.0380*	
H12W	0.06600	0.68980	0.27780	0.0380*	
H21W	0.22790	0.70540	0.62850	0.0710*	0.200
H22W	0.18990	0.52540	0.63450	0.0710*	0.200

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mg1	0.0232 (5)	0.0158 (5)	0.0167 (5)	0.0015 (4)	0.0003 (4)	-0.0012 (4)
F4	0.0271 (7)	0.0734 (12)	0.0671 (11)	0.0020 (8)	-0.0101 (7)	0.0008 (9)
O1	0.0388 (10)	0.0607 (12)	0.0412 (11)	0.0274 (9)	-0.0169 (8)	-0.0299 (9)
O1W	0.0261 (8)	0.0252 (8)	0.0249 (8)	0.0015 (7)	0.0008 (6)	0.0034 (6)
O21	0.0299 (8)	0.0197 (7)	0.0261 (8)	0.0051 (7)	-0.0011 (6)	-0.0065 (6)
O22	0.0274 (8)	0.0198 (7)	0.0186 (7)	0.0013 (6)	0.0003 (6)	-0.0028 (6)
C1	0.0310 (12)	0.0464 (15)	0.0286 (13)	0.0124 (12)	-0.0048 (10)	-0.0082 (11)
C2	0.0461 (16)	0.0655 (19)	0.0416 (16)	0.0250 (15)	-0.0107 (13)	-0.0223 (14)
C3	0.0373 (15)	0.0621 (18)	0.0457 (16)	0.0206 (14)	-0.0021 (12)	-0.0062 (14)
C4	0.0249 (12)	0.0519 (16)	0.0401 (15)	-0.0001 (12)	-0.0021 (11)	0.0062 (13)
C5	0.0354 (14)	0.0475 (16)	0.0383 (15)	-0.0048 (12)	-0.0037 (11)	-0.0096 (12)
C6	0.0334 (13)	0.0466 (15)	0.0327 (13)	0.0060 (12)	-0.0012 (11)	-0.0109 (12)
C11	0.0293 (12)	0.0258 (11)	0.0237 (11)	0.0069 (10)	-0.0005 (9)	-0.0071 (9)
C21	0.0254 (11)	0.0130 (9)	0.0198 (10)	-0.0022 (9)	0.0022 (8)	0.0013 (8)
O2W	0.045 (5)	0.054 (6)	0.043 (5)	-0.017 (5)	0.001 (4)	0.009 (4)

Geometric parameters (\AA , $^\circ$)

Mg1—O1W	2.1032 (14)	O2W—H21W	0.9500
Mg1—O21	2.0478 (14)	C1—C2	1.384 (4)
Mg1—O22 ⁱ	2.0620 (14)	C1—C6	1.379 (3)
Mg1—O1W ⁱⁱ	2.1032 (14)	C2—C3	1.381 (4)
Mg1—O21 ⁱⁱ	2.0478 (14)	C3—C4	1.356 (4)
Mg1—O22 ⁱⁱⁱ	2.0620 (14)	C4—C5	1.363 (4)
F4—C4	1.362 (3)	C5—C6	1.390 (3)

O1—C1	1.380 (3)	C11—C21	1.511 (3)
O1—C11	1.416 (3)	C2—H2	0.9300
O21—C21	1.257 (3)	C3—H3	0.9300
O22—C21	1.250 (3)	C5—H5	0.9300
O1W—H11W	0.9100	C6—H6	0.9300
O1W—H12W	0.9200	C11—H11B	0.9700
O2W—H22W	0.8500	C11—H11A	0.9700
O1W—Mg1—O21	90.96 (5)	C1—C2—C3	120.3 (3)
O1W—Mg1—O22 ⁱ	92.03 (5)	C2—C3—C4	118.7 (2)
O1W—Mg1—O1W ⁱⁱ	180.00	F4—C4—C3	118.7 (2)
O1W—Mg1—O21 ⁱⁱ	89.04 (5)	F4—C4—C5	118.7 (2)
O1W—Mg1—O22 ⁱⁱⁱ	87.97 (5)	C3—C4—C5	122.6 (2)
O21—Mg1—O22 ⁱ	84.33 (5)	C4—C5—C6	119.0 (2)
O1W ⁱⁱ —Mg1—O21	89.04 (5)	C1—C6—C5	119.6 (2)
O21—Mg1—O21 ⁱⁱ	180.00	O1—C11—C21	109.90 (17)
O21—Mg1—O22 ⁱⁱⁱ	95.67 (5)	O21—C21—C11	115.38 (19)
O1W ⁱⁱ —Mg1—O22 ⁱ	87.97 (5)	O22—C21—C11	119.32 (18)
O21 ⁱⁱ —Mg1—O22 ⁱ	95.67 (5)	O21—C21—O22	125.3 (2)
O22 ⁱ —Mg1—O22 ⁱⁱⁱ	180.00	C3—C2—H2	120.00
O1W ⁱⁱ —Mg1—O21 ⁱⁱ	90.96 (5)	C1—C2—H2	120.00
O1W ⁱⁱ —Mg1—O22 ⁱⁱⁱ	92.03 (5)	C2—C3—H3	121.00
O21 ⁱⁱ —Mg1—O22 ⁱⁱⁱ	84.33 (5)	C4—C3—H3	121.00
C1—O1—C11	117.06 (19)	C4—C5—H5	120.00
Mg1—O21—C21	139.08 (14)	C6—C5—H5	121.00
Mg1 ^{iv} —O22—C21	132.00 (13)	C5—C6—H6	120.00
Mg1—O1W—H12W	103.00	C1—C6—H6	120.00
H11W—O1W—H12W	114.00	O1—C11—H11A	110.00
Mg1—O1W—H11W	123.00	O1—C11—H11B	110.00
H21W—O2W—H22W	102.00	C21—C11—H11B	110.00
O1—C1—C6	124.9 (2)	H11A—C11—H11B	108.00
C2—C1—C6	119.9 (2)	C21—C11—H11A	110.00
O1—C1—C2	115.2 (2)		
O1W—Mg1—O21—C21	36.0 (2)	C6—C1—C2—C3	-0.2 (4)
O22 ⁱ —Mg1—O21—C21	127.9 (2)	O1—C1—C6—C5	-179.4 (2)
O1W ⁱⁱ —Mg1—O21—C21	-144.0 (2)	C2—C1—C6—C5	-0.3 (4)
O22 ⁱⁱⁱ —Mg1—O21—C21	-52.1 (2)	C1—C2—C3—C4	0.7 (4)
C11—O1—C1—C2	-175.1 (2)	C2—C3—C4—F4	178.5 (2)
C11—O1—C1—C6	4.0 (3)	C2—C3—C4—C5	-0.7 (4)
C1—O1—C11—C21	169.15 (19)	F4—C4—C5—C6	-179.0 (2)
Mg1—O21—C21—O22	-136.10 (18)	C3—C4—C5—C6	0.2 (4)
Mg1—O21—C21—C11	43.1 (3)	C4—C5—C6—C1	0.3 (4)
Mg1 ^{iv} —O22—C21—O21	4.0 (3)	O1—C11—C21—O21	172.84 (18)
Mg1 ^{iv} —O22—C21—C11	-175.24 (13)	O1—C11—C21—O22	-7.9 (3)
O1—C1—C2—C3	179.0 (2)		

Symmetry codes: (i) $-x, y+1/2, -z+1/2$; (ii) $-x, -y+1, -z+1$; (iii) $x, -y+1/2, z+1/2$; (iv) $-x, y-1/2, -z+1/2$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D\cdots H$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H11W···O1 ^v	0.91	2.45	3.214 (2)	143
O1W—H12W···O22 ^v	0.92	2.38	3.0352 (19)	128
O1W—H12W···O21 ⁱ	0.92	1.92	2.760 (2)	151
O2W—H21W···O1 ^v	0.95	2.41	3.034 (10)	123
O2W—H22W···O22 ⁱⁱⁱ	0.85	2.13	2.950 (9)	160

Symmetry codes: (i) $-x, y+1/2, -z+1/2$; (iii) $x, -y+1/2, z+1/2$; (v) $x, y+1, z$.